

Vibrational Spectroscopy of H₂O by Lie Algebraic Methods

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An algebraic model of coupled anharmonic oscillators is introduced, capable of describing the stretching vibrations of medium-size molecules. This model is applied to the calculation of O–H vibrational modes of water molecules. In this paper, we have reported the stretching and bending vibrational energy levels of water molecule using the algebraic and density functional theory method. The results obtained by theoretical models show good agreement with the experimental values.

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1. Introduction

A new theoretical concept — vibron model (based on the Lie algebra) to study molecular spectra was built in the last part of the 20th century [1, 2]. This new model seems to offer a concrete and complementary technique to the traditional approaches used in molecular spectroscopy. The algebraic model (vibron model) originally developed for diatomic and tri-atomic molecules [3, 4]. U(4) and U(2) algebraic models have been used so far in the analysis of experimental data. The U(4) model deals with the rotation and the vibration simultaneously, but it becomes quite complicated when the number of atoms in a molecule are more than four. The U(2) model was particularly successful in explaining stretching vibrations of linear and bent X₂Y molecules [5–7]. Later, it extended to linear and quasi-linear tetra atomic molecules [8–10] and could prove itself to be a competitive one to the traditional analysis. The main features and basic applications of these methods have been described by Iachello and Levine [11] and Oss. The Lie algebraic approach was found to be successful in our study of the vibrational spectra of H₂O and CF₄ [12], HCN [13], HCCF, HCCD [14], tetrahedral [15], nickel metalloporphyrins [16], copper tetramesityl porphyrin [17]. Highly accurate prediction of molecular vibrations has been a challenging task since ever in theoretical and physical chemistry. Quantum chemistry allows currently, valuable estimations of vibrational energy levels, one of the best and recent advanced is density functional theory (DFT) method [18].

In this paper, we use the U(2) algebraic model to calculate the normal fundamental and overtone modes of

vibrations of water molecule and hence find the accuracy of the results with respect to the experimental observations.

2. Algebraic framework

The algebraic model is based on the isomorphism of the U(2) Lie algebra and one-dimensional Morse oscillator whose eigenstates may be associated with U(2) ⊃ O(2) states. For a tri-atomic molecule like A₂B, we introduce two U(2) Lie algebra to describe two stretching bonds (A–B) respectively. Two possible chains of molecular dynamical groups in tri-atomic molecules are described by

$$U_1(2) \otimes U_2(2) \supset O_1(2) \otimes O_2(2) \supset O_{12}(2) \quad (1)$$

$$\text{q.n. : } N_1 \quad N_2 \quad n \quad m \quad n+m$$

$$U_1(2) \otimes U_2(2) \supset U_{12}(2) \supset O_{12} \quad (2)$$

$$\text{q.n. : } N_1 \quad N_2 \quad \nu_1 + \nu_2$$

where Eqs. (1) and (2) correspond to local and normal coupling, respectively. The quantum numbers corresponding to various algebras are indicated by n, m in Eq. (1) and ν_1, ν_2 in Eq. (2). N_1 and N_2 are vibron numbers corresponding to the number of bound states of two oscillators and are constant for the system. It is to be noted here that $n+m = \nu_1 + \nu_2$ is a conserved quantity. The bending motion can now be assigned an algebra U₃(2) to be combined with the algebra U₁(2) ⊗ U₂(2) associate with the interacting stretching motions.

The common algebraic model Hamiltonian in the case of stretching and bending mode for molecule we consider thus has the form [11]:

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i<j}^n A_{ij} C_{ij} + \sum_{i<j}^n \lambda_{ij} M_{ij}. \quad (3)$$

In this expression, one finds three different classes of effective contributions. The first one, $\sum_{i=1}^n A_i C_i$ is devoted to the description of n independent, anharmonic

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sequences of vibrational levels (associated with n independent, local oscillators) in terms of the operators C_i . The second one, $\sum_{i<j}^n A_{ij}C_{ij}$ leads to cross-anharmonicities between pairs of distinct local oscillators in terms of the operators C_{ij} . The third one, $\sum_{i<j}^n \lambda_{ij}M_{ij}$ describes anharmonic, non-diagonal interactions involving pairs of local oscillators in terms of the operators M_{ij} . In Eq. (3), C_i is an invariant operator with eigenvalues $4(\nu_i^2 - N_i\nu_i)$ and matrix elements with the Casimir and Majorana operators are as follows:

$$\begin{aligned} \langle N_i, \nu_i; N_j, \nu_j | C_{ij} | N_i, \nu_i; N_j, \nu_j \rangle \\ = 4[(\nu_i + \nu_j)^2 - (\nu_i + \nu_j)(N_i + N_j)], \end{aligned} \quad (4)$$

$$\begin{aligned} \langle N_i, \nu_i; N_j, \nu_j | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle \\ = N_i\nu_j + N_j\nu_i - 2\nu_i\nu_j, \end{aligned} \quad (5)$$

$$\begin{aligned} \langle N_i, \nu_i + 1; N_j, \nu_j - 1 | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle \\ = -[\nu_j(\nu_i + 1)(N_i - \nu_i)(N_j - \nu_j + 1)]^{1/2}, \end{aligned} \quad (6)$$

$$\begin{aligned} \langle N_i, \nu_i - 1; N_j, \nu_j + 1 | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle \\ = -[\nu_i(\nu_j + 1)(N_j - \nu_j)(N_i - \nu_i + 1)]^{1/2}. \end{aligned} \quad (7)$$

3. Results and discussion

A comparison of the experimental and calculated frequencies of stretching and bending vibrations of water molecule using the algebraic model is shown in Table I. Using established norms [10, 15], the vibron number N and other algebraic parameters A , A , k , k_0 are shown in Table II for water molecule.

The optimized configuration of water is shown in Fig. 1.

Vibrational energy levels (in cm^{-1}) of H_2O .

TABLE I

$(\nu_1 \nu_2 \nu_3)$	Observed (I)	Calculated		Deviation	
		Algebraic method	DFT method	Δ	δ
(1 0 0)	3657.05	3657.80	3737.96	-0.75	-80.91
(0 0 1)	3755.93	3747.56	3869.96	8.37	-114.03
(2 0 0)	7201.54	7155.08	-	23.23	32.85218
(1 0 1)	7249.82	7244.48	-	2.67	3.77595
(0 0 2)	7445.05	7484.04	-	19.495	27.57009
(3 0 0)	10599.66	10580.76	-	9.45	13.36432
(2 0 1)	10613.41	10668.24	-	27.415	38.77066
(1 0 2)	10868.86	10794.43	-	37.215	52.62996
(0 0 3)	11032.40	11057.60	-	12.6	17.81909
(2 0 2)	13828.30	13665.93	-	81.185	114.81293
(3 0 1)	13830.92	13843.40	-	6.24	8.82469
(4 0 0)	14221.14	14211.45	-	4.845	6.85186
(1 0 3)	14318.80	14468.23	-	74.715	105.66297
(0 0 4)	14536.87	14536.44	-	0.215	0.30406
(3 0 2)	16898.40	16895.67	-	-	-
(4 0 1)	16898.83	16899.78	-	-	-
(5 0 0)	17458.20	17455.88	-	-	-
(2 0 3)	17495.52	17498.56	-	-	-
(1 0 4)	17748.07	17750.55	-	-	-
(0 0 5)	17970.90	17970.54	-	-	-
(4 0 2)	-	19880.40	-	-	-
(5 0 1)	-	19962	-	-	-
(6 0 0)	-	20292.79	-	-	-
(3 0 3)	-	20555.96	-	-	-
(2 0 4)	-	20833.07	-	-	-
(1 0 5)	-	21077.64	-	-	-
(0 0 6)	-	21256.28	-	-	-

3.1. Experimental data

Reference [5] provides the necessary experimental data for this study.

3.2. Vibron number

In algebraic theory, we introduce the vibron number N which is directly related to the anharmonicity of the

local O-H stretching bonds. The value of vibron number N_i (for stretching bond) for H_2O molecule can be determined by the relation [11]:

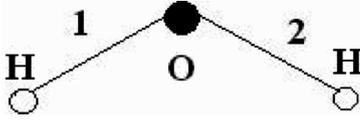
$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \quad (8)$$

where ω_e and $\omega_e x_e$ are the spectroscopic constants of

TABLE II

Algebraic parameters for H_2O . All parameters are in cm^{-1} except N , which is dimensionless.

Stretching parameters	Bending parameters
$N_1 = N_2 = N = 44$	$N_3 = 28$
$A_1 = A_2 = A = -18.98$	$A_3 = -14.76$
$A_{12} = -1.13$	$A_{13} = A_{23} = -3.62$
$\lambda_{12} = 1.04$	$\lambda_{13} = \lambda_{23} = 1.72$

Fig. 1. Optimized structure of H_2O molecule.

stretching interactions of diatomic molecules considered. From Fig. 1, it can be noticed that some of the bonds are equivalent. It may be noted that during the calculation of the vibrational frequencies of water molecule, the value of N is kept fixed and not used as a free parameter.

This numerical value must be seen as initial guess; depending on the specific molecular structure, one can expect changes in such an estimate, which, however, should not be larger than $\pm 20\%$ of the original value.

3.3. Values of the fitting parameters

The fitting parameters A, A', λ, N which are used in this study for the vibrational frequencies of water molecule for 44 stretching vibrational bands are given in the following Table II.

For a tri-atomic molecule H_2O , we number the bonds from 1 to 3. It is seen that two stretching bond A-B from 1 to 2 are equivalent. Thus we choose the parameters for stretching bond as $N_i = N_1 = N_2 = N$, $A_i = A_1$ (for $i = 1$ to 2), $A_{ij} = A_{12}$ and $\lambda_{ij} = \lambda_{12}$ (for $i, j = 1, 2$). The parameters λ_{ij} describe the interactions between stretching bonds and the interaction between bending bond, respectively. The fitting parameters [12] used in the study of vibrational spectra of water molecule are given in Table II.

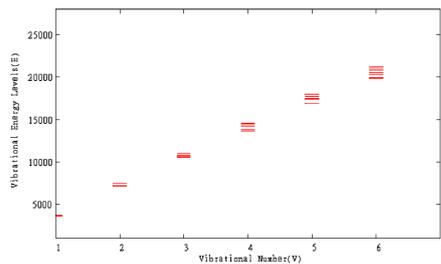


Fig. 2. O-H band vibrational energy levels of water.

The highly excited vibrational levels, calculated by using the algebraic Hamiltonian Eq. (3), are shown in Fig. 2 (the calculated in detail vibrational energy levels are listed in Table I). When the quantum number ν increases in a fixed band, the degeneracy of energy levels increase rapidly. Usually, the degeneracy or anti-degeneracy of energy levels is called clustering. It may

be seen from Fig. 2 that the vibrational energy levels of water molecule form make up clusters.

4. Conclusion

We have presented here a vibrational analysis of the stretching modes of water molecule in terms of one-dimensional vibron model. The parameters of O-H bonds have been determined by a fit to the known states of H_2O , while the interactions between different modes have been estimated. The calculation provides complete analysis of some of the stretching modes of water molecule (we have the calculation also for the remaining modes). The importance of the method is that it allows one to do a global analysis of all molecular species in terms of few parameters. The present calculation demonstrates that $U(2)$ model can be applied successfully to the higher excited states of water molecules. In turn it provides way to make assignments of unknown levels or to check assignments of known levels.

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